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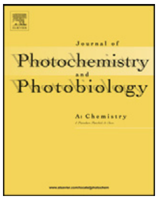

Spectroscopic study of intramolecular energy transfer in a phosphine oxide Eu^{3+} complex: A stepwise process induced by intermediate energy levels

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ABSTRACT

The intramolecular energy transfer process in a ternary Europium(III) complex $Eu(TTA)_3(TAPO)_2$ (**1**, TAPO = (4-diphenylamine-phenyl)-diphenylphosphine oxide, TTA = 2-thenoyltrifluoroacetonate) was investigated with both steady-state and time-resolved spectroscopic approaches to figure out the detail of the energy transfer between the neutral and anion ligands. The energy transfer from the first singlet excited energy level (S_1) of the anion ligand TTA to the first triplet excited energy level (T_1) of TAPO was first proved. This discovery supports that when the neutral ligand has an appropriate T_1 level between the S_1 and T_1 levels of the anion ligand, the energy can be transferred from the S_1 energy level of the neutral ligands to $^5D_0$ of Eu^{3+} through a stepwise process: $S_1^{TAPO} \rightarrow S_1^{TTA} \rightarrow T_1^{TAPO} \rightarrow T_1^{TTA} \rightarrow {}^5D_0^{Eu^{3+}}$. This kind of sequential process makes intramolecular energy transfer more efficient, and is one of the most important factors resulting in the great improved photoluminescent performance of **1**. It is shown that in ternary lanthanide complexes the efficient energy transfer between the neutral and anion ligands is crucial to the luminescent performance of the complex. And the intramolecular energy transfer can be facilitated by the ladder-like distribution of the excited energy levels.

1. Introduction

The properties of the excited lanthanide complexes, which are important for the theoretical and applied researches, have been studied extensively for decades. Much attention is paid to the intramolecular energy transfer processes, since they can indicate the effects of ligands in the emission processes and give proper guidance in choosing and designing ligands in bright light-emitting lanthanide complexes. The intramolecular energy transfer mechanisms of binary systems, which consist of the anion ligands and lanthanide ions, are studied by Weissman, Dexter, Crosby and other scientists. One of the most important mechanisms is that anion ligands are excited to their first singlet excited energy levels (S_1), then the energy transfers to the first triplet excited energy levels (T_1). Subsequently, the energy transfers to the excited energy levels of lanthanide ions, and finally the molecules give out the characteristic emissions of lanthanide ions [1–10].

In recent years, ternary lanthanide complexes, which consist of neutral ligands, anion ligands and lanthanide ions, become attractive as electroluminescent (EL) materials with the highest colour purity [11]. It is found that both of the neutral and anion ligands play very important role in the light-emitting processes. To improve the EL performances, much attention has been paid to the modification of the ligands in two aspects: improving their carrier injection and transporting ability [12–15] and tuning their excited energy levels to fit lanthanide ions [16–18]. With the substitution of carrier injection/transporting moieties, the corresponding ability of the ligands and complexes can be tuned conveniently. However, the EL performance of these complexes is still worse than expected. Inefficient intramolecular energy transfer seems to be one of the main constraints [11]. Actually, since the ternary systems are much more complicated than the binary systems, it is much more difficult to achieve the efficient energy transfer between neutral ligands, anion ligands and lanthanide ions purposefully. Therefore, the study of intramolecular energy transfer mechanism of ternary lanthanide complexes becomes significant to the molecular design of the complexes. Huang and her coworkers have studied the effect of different neutral ligands, such as triphenylphosphine oxide (TPPO) and 1,10-phenanthroline (phen), on the luminescent properties of ternary pyrazolone terbium^{III} and europium^{III} complexes [17,18]. The efficient antenna effect of the neutral ligands and the positive energy

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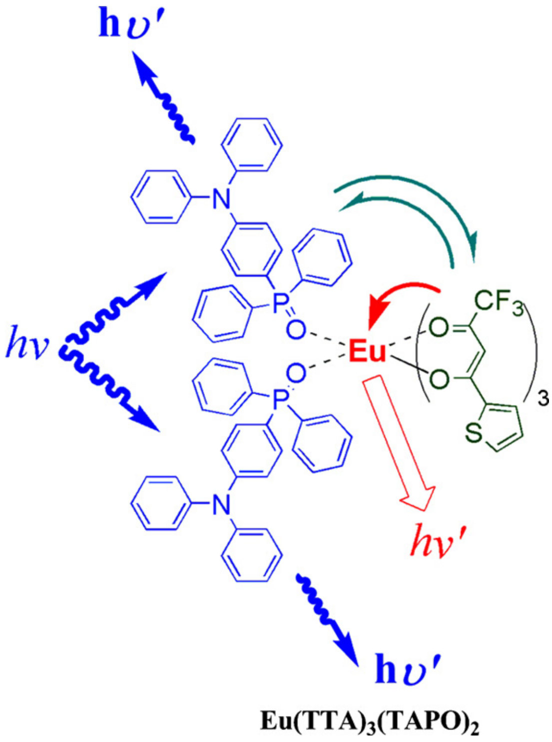


Scheme 1. Molecular structure of Eu(TTA)$_3$(TAPO)$_2$, **1**.

transfer from neutral ligands to anion ligands are proved to be significant to the favourable luminescent performances. However, because the T_1 levels of TPPO and phen are equivalent to or lower than those of the corresponding pyrazolones, this study is not yet comprehensive. Moreover, there are few works trying to study the detail process of intramolecular energy transfer in ternary lanthanide complexes [9]. Especially, how the energy transfer between the S_1 and T_1 levels of the neutral and anion ligands is still not very clear. The generally applicable mechanism of the intramolecular energy transfer would be very useful for finely and purposefully tuning the excited energy levels of the neutral ligands. Our previous work showed that the introduction of aryl phosphine oxide ligands, such as Bis(2-(diphenylphosphino)phenyl) ether oxides (DPEPO) [20] and TAPO [21] can greatly increase the photoluminescent quantum yield (PLQY) of their Eu^{3+} complex. Although in the previous works the possible intramolecular energy transfer mechanism was proposed, and the intermediate T_1 level of these neutral ligands between the S_1 and T_1 levels of the anion ligand was believed to be one of the most important factors resulting in the improvement, It was still insufficient that the detail of the energy transfer between neutral and anion ligands was not clear.

In the present paper, in order to pinpoint the intramolecular energy transfer mechanism of ternary Eu^{3+} complexes and the relationship between neutral and anion ligands in the energy transfer process, we chose a monodentate aryl phosphine oxide Eu^{3+} complex Eu(TTA)$_3$(TAPO)$_2$ (**1**, TAPO is (4-diphenylamine-phenyl)-diphenyl-phosphine oxide as the neutral ligand, TTA is 2-thenoyltrifluoroacetonate as the anion ligand, Scheme 1), whose neutral-ligand-localized fluorescence and phosphorescence are visible at room temperature. On the basis of our previous works [19], herein we focused on the energy transfer between neutral and anon ligands, especially the potential energy transfer between S_1 level of TTA and T_1 level of TAPO. And according to the spectroscopic study of this complex, a continuous stepwise intramolecular energy transfer mechanism of ternary Europium complexes is proposed and discussed in detail.

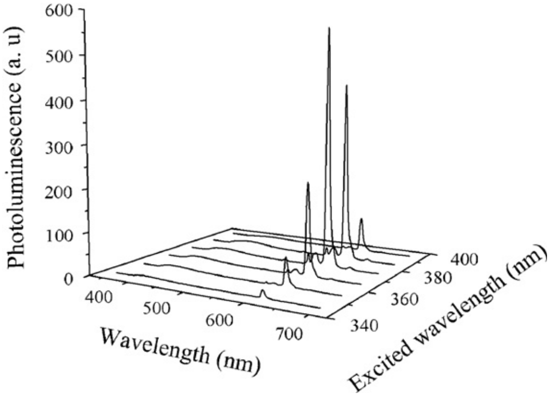


Fig. 1. The excitation spectra of TAPO and Eu(TTA)$_3$(TAPO)$_2$.

2. Experimental

2.1. Materials

All the reagents and solvents used for the synthesis of Eu(TTA)$_3$(TAPO)$_2$ **1** were purchased from Aldrich and Acros companies. All the reagents were used without further purification. The molecular structure and synthetic procedure of **1** is shown in Scheme 1. The synthetic approaches were according to our previous work [19]. ESI/MS (*m*/*z*): 1706 (M^+, 51%), 1260 (23%), 815 (21%), 445 ($TAPO^+$, 100%).

2.2. Methods

Absorption, excitation and photoluminescence (PL) emission spectra of the target compound were measured in dichloromethane using a SHIMADZU UV-3150 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. The concentrations of the solutions are 10^{-5} mol l^{-1} in order to eliminate the concentration quenching. Time-resolved and phosphorescence spectra were measured in dichloromethane using an Edinburgh FPLS 920 fluorescence spectrophotometer at room temperature or 77 K cooling by liquid nitrogen. The time-resolved measurements were performed using Time-Correlated Single Photon Counting (TCSPC) method with a nF900 nanosecond flash lamp for 100 ps–10 μs lifetime measurement, a microsecond pulsed Xenon light source for 10 μs–10 s lifetime measurement, and the synchronization photomultiplier for signal collection and the Multi-Channel Scaling Mode of the PCS900 fast counter PC plug-in card for data processing. Since the lifetimes of the phosphorescence from TAPO in **1** are close to the lower measurement bound of the flash light source, the instrument response function (IRF) is measured together with the decay profiles to improve the accuracy.

3. Results and discussion

The absorption spectrum of **1** in dilute CH_2Cl_2 solutions (1×10^{-5} mol l^{-1}) were measured (SI 1). The spectrum contains a wide bond from 250 to 400 nm with the maximum at 333 nm, which is contributed by both TAPO and TTA. The PL spectra of **1** in dilute CH_2Cl_2 solutions (1×10^{-5} mol l^{-1}) with the different excitation wavelengths from 340 to 390 nm were measured (Fig. 1). There are two sets of emissions in all of the spectra. The first set contains four peaks at 579, 593, 611, and 653 nm corresponding to the characteristic emissions from Eu^{3+} attributed to $^5D_0$–^7F_j (j = 0–3) transitions. And the second set consists of blue emissions with the range from 350 to 500 nm. Both of the emissions at 579 and 593 nm are single peaks. Therefore, the coordination environment of Eu^{3+}

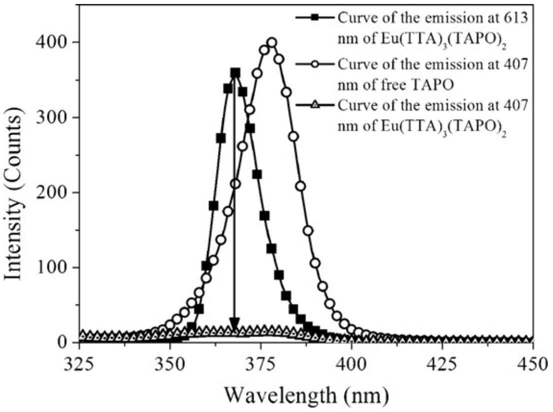
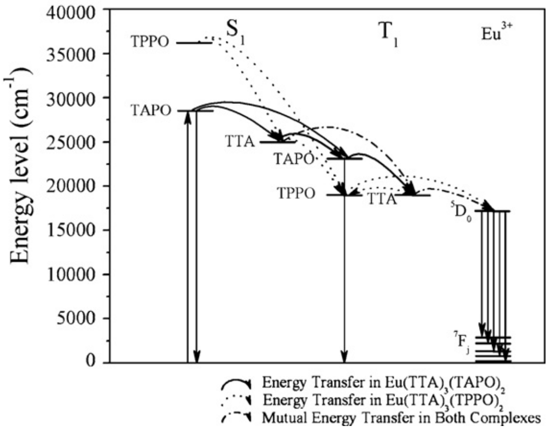


Fig. 2. The photoluminescence spectra of **1** excited by different wavelength lights.



Scheme 2. The energy level schemes of **1** and Eu(TTA)$_3$(TPPO)$_2$.

is unique [22]. It implies that in the dilute solution **1** retains the stable ternary complex structure. Nevertheless, the weaker peak at the wavelength range from 350 to 500 nm is recognized as the emission of TAPO, whose fluorescent and phosphorescent emission peaks are at 407 and 433 nm, respectively [19]. This should be induced by both the bigger volume and degree of freedom of TAPO, which make the structure of **1** more incompact and consequently reduce the energy transfer efficiency between TAPO and Eu^{3+}. Thus, the emissions of TAPO (including fluorescence and phosphorescence) become visible. It is noticeable that although the emission of TAPO in **1** implies the incomplete energy transfer, the relative PLQY of **1** was 39.4% [19], which is about 1.5 times of that of the reference complex Eu(TTA)$_3$(TPPO)$_2$ (26.7%) [17].

The absorption and PL spectra of TAPO and TTA in dilute CH_2Cl_2 solutions (1×10^{-5} mol l^{-1}) were shown in SI 2. TAPO has the bright blue emission with the peak at 407 nm (excited by 310 nm). The absorption edges of TAPO and TTA are 375 nm and 398 nm, respectively. The PL spectra of Gd(NO$_3$)$_3$(TAPO)$_2$ and Gd(TTA)$_3$(H$_2$O)$_2$ were measured to determine the phosphorescent emissions of TAPO and TTA in the complex.[14] The phosphorescent peaks are at 433 nm (for TAPO) and 527 nm (for TTA) (SI 2).

The excitation spectra of free TAPO in CH_2Cl_2 (2×10^{-5} mol l^{-1}), TAPO in **1** (the blue emission of **1** around 407 nm) and Eu^{3+} in **1** (the red emissions of **1** around 611 nm) in CH_2Cl_2 (1×10^{-5} mol l^{-1}) were measured to study the effect of TAPO in the intramolecular energy transfer process (Fig. 2). Free TAPO has a strong excitation peak from 350 to 380 nm. However, for **1**, when 407 nm was set as the emission wavelength, it is showed that no distinct peak was found at the same range. Furthermore, when setting 611 nm as the emission wavelength, a strong excitation peak was observed at the similar range from 350 to 390 nm. It is noticed that this bond is stronger and shifts red slightly compared with the absorbance bond of free TAPO, which is induced by the contribution from TTA. It means that nearly all of the energy of TAPO transfers to Eu^{3+}, and Eu^{3+} obtains energy mainly from TAPO. It is no doubt that in the complex TAPO mainly plays the role of absorbing and transferring energy, which is known as "antenna effect".

According to the excited energy levels of TAPO, TPPO and TTA [18], the more appropriate S$_1$ and T$_1$ levels of TAPO than those of TPPO may induce the improved energy transfer between the corresponding energy levels of neutral ligands and anion ligands (Scheme 2). It is obvious that one of the most important drawbacks of TPPO is its too high S$_1$ level and too low T$_1$ level, which may remarkably decrease the energy transfer efficiencies. Moreover, it is noticeable that the T$_1$ level of TAPO is between the S$_1$ and T$_1$ levels of TTA, which probably makes the T$_1$ level of TAPO seem like a transition level in the intramolecular energy transfer process. The principal goal of this study was to prove the potential of the energy transfer between S$_1$ level of TTA and T$_1$ level of TAPO. With this critical link, the intramolecular energy transfer in **1** would be a continuous stepwise process.

A small detail of PL spectra of **1** was noticed that along with the increasing of the excitation wavelength, the peaks at short wavelengths (originated from TAPO) shift red gradually (Fig. 1). Fig. 3 shows the results of the multi-peak fitting of these blue emission peaks. It is very clear that these peaks can be divided into two peaks at 407 and 433 nm, which correspond to the fluorescence ($FL_{TAPO\mathbf{1}}$) and phosphorescence ($Ph_{TAPO\mathbf{1}}$) of TAPO in **1**, respectively. Significantly, along with the increasing of the excitation wavelength, the proportion of $Ph_{TAPO\mathbf{1}}$ gradually increases and the proportion of $FL_{TAPO\mathbf{1}}$ decreases. Obviously, if all of the T$_1$ energy of TAPO was transferred from the S$_1$ level of TAPO, the intensity ratio of $FL_{TAPO\mathbf{1}}$ to $Ph_{TAPO\mathbf{1}}$ should be a constant. Thus, there must be other energy transfer channels for the T$_1$ energy of TAPO. The PL spectrum of **1** with the excitation wavelength of 385 nm gives the answer (Fig. 3). Since the absorption edge of TAPO is 375 nm, TAPO in **1** cannot be excited by 385 nm. It is found that this blue emission with the peak at 433 nm is the pure phosphorescence of TAPO. In the complex, only TTA can be excited by 385 nm. It is also showed that the excitation spectrum of $Ph_{TAPO\mathbf{1}}$ can be divided into two parts, one is contributed by TAPO and the other is attributed to TTA (SI 3). It means that in this case TTA is firstly excited to its S$_1$ level, and then energy transfers to the T$_1$ level of TAPO. Part of this T$_1$ energy is released as $Ph_{TAPO\mathbf{1}}$. It proves that the energy can be transferred

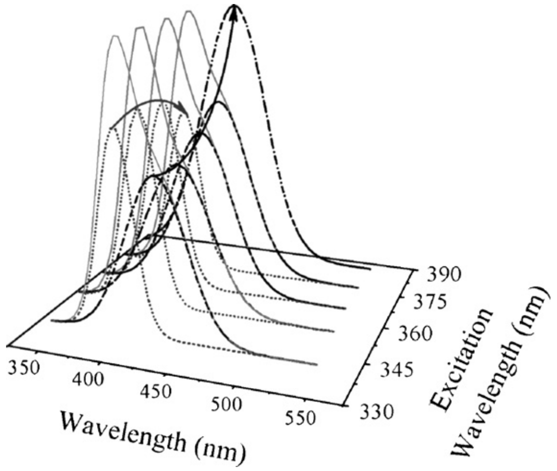


Fig. 3. The consistence of the blue emissions of **1**: fluorescence (dot lines) and phosphorescence of TAPO in **1** (dash dot lines).

Table 1
The lifetimes of emissions of TAPO and Eu^{3+} in **1** at different excitation wavelengths.

Excitation wavelength (nm)	Lifetime (μs)			
	433 nm of **1**	$Gd(NO_3)_3(TAPO)_2$	611 nm of **1**	$Eu(TTA)_3{\cdot}2H_2O$
340	0.88 (83.12%) 10.09 (16.88%)	3.86 (33.87%) 15.15 (66.13%)	410.59	56.25 (37.88%) 314.26 (62.12%)
360	0.40 (85.46%) 7.40 (14.50%)	–	409.82	–
380	0.16 (94.89%) 7.70 (5.11%)	–	407.87	–
400	0.17 (96.50%) 7.50 (3.50%)	–	405.15	–

from the S_1 level of TTA to the T_1 level of TAPO. With this important link, the entire energy transfer process in **1** is very likely to be a sequential and stepwise process.

It is assumed that the T_1 energy of TAPO originates from the higher energy levels, including S_1 levels of TAPO and TTA. Since the S_1 energy of TTA can be divided into two parts: one ascribes the energy transfer from S_1 level of TAPO, the other is absorbed by TTA itself, the overall T_1 energy of TAPO ($E_{T_1\cdot TAPO}$) includes three components of $E_{S_1\cdot TAPO\to T_1\cdot TAPO}$, $E_{S_1\cdot TAPO\to S_1\cdot TTA\to T_1\cdot TAPO}$ and $E_{S_1\cdot TTA\to T_1\cdot TAPO}$ as the following:

$$E_{T_1\cdot TAPO} = E_{S_1\cdot TAPO\to S_1\cdot TTA\to T_1\cdot TAPO} + E_{S_1\cdot TAPO\to T_1\cdot TAPO} + E_{S_1\cdot TTA\to T_1\cdot TAPO} \quad (1)$$

The subscripts indicate their different energy transfer processes. For $E_{S_1\cdot TAPO\to T_1\cdot TAPO}$ and $E_{S_1\cdot TAPO\to S_1\cdot TTA\to T_1\cdot TAPO}$, the starting point of the processes is the S_1 level of TAPO. Then one part of the energy transfers to the T_1 level of TAPO directly (for the former), while another part of the energy transfers to the T_1 level of TAPO through the S_1 level of TTA as the transition level (for the latter). For $E_{S_1\cdot TTA\to T_1\cdot TAPO}$, TTA firstly absorbs energy by itself and is excited to its S_1 level, and then the energy transfers to the T_1 level of TAPO. It is obvious that $E_{S_1\cdot TAPO\to T_1\cdot TAPO}$ and $E_{S_1\cdot TAPO\to S_1\cdot TTA\to T_1\cdot TAPO}$ depend on the S_1 energy of TAPO, however, $E_{S_1\cdot TTA\to T_1\cdot TAPO}$ is only related with the S_1 energy absorbed by TTA rather than TAPO. In the wavelength range from 300 to 350 nm, the absorption of TAPO is much stronger than that of TTA. Accordingly, $E_{S_1\cdot TAPO\to T_1\cdot TAPO}$ and $E_{S_1\cdot TAPO\to S_1\cdot TTA\to T_1\cdot TAPO}$ are predominant than $E_{S_1\cdot TTA\to T_1\cdot TAPO}$. Thus, the proportions of $FL_{TAPO\mathbf{1}}$ and $Ph_{TAPO\mathbf{1}}$ are relatively constant. Along with the increasing of the excited wavelength (more than 360 nm), the absorption of TAPO reduces quickly, which results in the decrease of all kinds of the excited energy related to the S_1 energy of TAPO, including the intensity of $FL_{TAPO\mathbf{1}}$, $E_{S_1\cdot TAPO\to T_1\cdot TAPO}$ and $E_{S_1\cdot TAPO\to S_1\cdot TTA\to T_1\cdot TAPO}$. However, $E_{S_1\cdot TTA\to T_1\cdot TAPO}$ is independent on the S_1 energy of TAPO, and therefore, becomes the main component of the T_1 energy of TAPO. Thus, along with the increasing of the excited wavelength, $FL_{TAPO\mathbf{1}}$ would quickly decrease, while $Ph_{TAPO\mathbf{1}}$ would be relatively stable. Intensity of $Ph_{TAPO\mathbf{1}}$ would gradually exceed that of $FL_{TAPO\mathbf{1}}$ and finally only $Ph_{TAPO\mathbf{1}}$ could be observed.

In parallel with the steady-state experiments, time-resolved spectroscopic properties of **1** were also investigated in detail. The data are listed in Table 1. For comparison, we also measured the decay curve of $Eu(TTA)_3{\cdot}2H_2O$, which is doubly-exponential (Fig. 4). This complex has two lifetimes of 56.25 and 314.26 μs. The longer one corresponds to the energy transfer process involving in the S_1 and T_1 levels of TTA and $^5D_0$ of Eu^{3+}. The shorter one should be attributed to water-induced quenching. Contrarily, the decay curves of **1** with different excitation wavelengths are single-exponential. With the excitation wavelength of 340 nm, the lifetime of **1** is 410.59 μs, which is 100 μs longer than that of $Eu(TTA)_3{\cdot}2H_2O$ (Fig. 4).

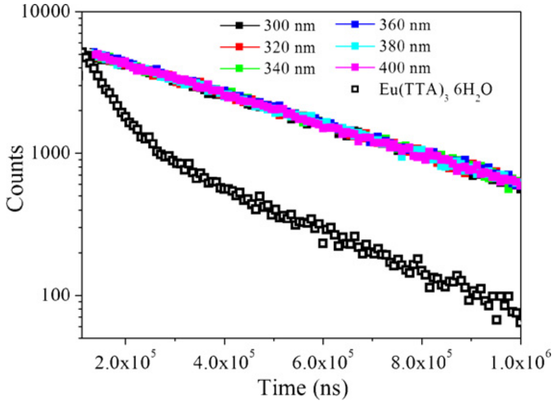


Fig. 4. Decay curves of the Eu^{3+} emission of **1** and $Eu(TTA)_3{\cdot}2H_2O$ at different excitation wavelengths.

Decay curves of $Ph_{TAPO\mathbf{1}}$ and $Gd(NO_3)(TAPO)_2$ were also measured (Fig. 5 and Table 1). All of these curves are doubly-exponential. $Gd(NO_3)_3(TAPO)_2$ has two lifetimes of 3.86 and 15.15 μs. The longer one, which is dominant, corresponds to the normal decay of the T_1 state of TAPO. The shorter one should be induced by the quenching effect of the neighbouring nitrates. Compared with $Gd(NO_3)(TAPO)_2$, the lifetimes of $Ph_{TAPO\mathbf{1}}$ are much shorter. Although it also has two lifetimes, the shorter one (τ_{Sh}) becomes dominant to the longer one (τ_L). Obviously, the shorter lifetimes of $Ph_{TAPO\mathbf{1}}$ should be induced by the more rapid and efficient energy transfer between the T_1 level of TAPO and the T_1 level of TTA or $^5D_0$ of Eu^{3+}. τ_{Sh} with the excitation wavelength of 340 nm is 0.88 μs. However, when the excitation wavelength is 360 nm, it becomes much shorter as 0.4 μs. When the excitation wavelength exceeds the absorption edge of TAPO, such as 380 and 400 nm, τ_{Sh} becomes much more preponderant with the proportions over 90% and tends to be a constant of 0.17 μs.

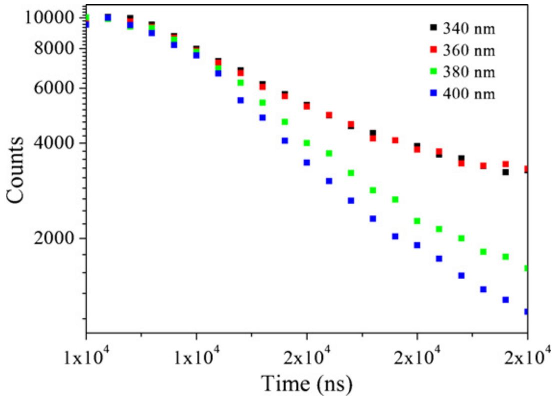


Fig. 5. Decay curves of the phosphorescent emission of TAPO in **1** at different excitation wavelengths.

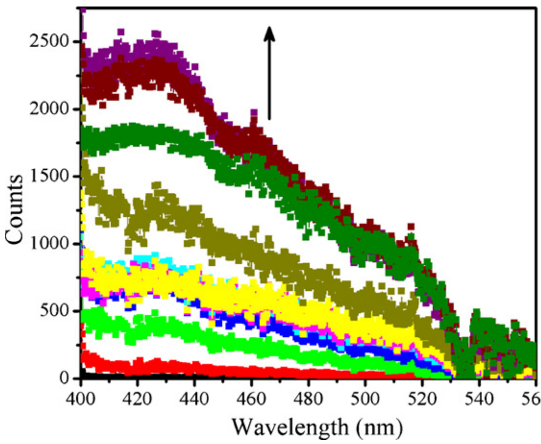


Fig. 6. Time-resolved emission spectra of **1** in CH_2Cl_2 between 0 and 200 ns with a time interval of 20 ns and the excitation wavelength of 380 nm at room temperature.

Although all of the results prove the energy transfer from the S_1 level of TTA to the T_1 level of TAPO, the time-resolved emission spectra (TRES) of **1** with the time range from 0 to 200 ns were measured to find out the direct evidences. In order to get rid of the interference of the S_1 level of TAPO, the excitation wavelength was chosen as 380 nm. It is found that although TAPO cannot be directly excited by 380 nm, $Ph_{TAPO\mathbf{1}}$ becomes stronger and stronger in the initial one hundred nanoseconds (Fig. 6). Obviously, this triplet energy of TAPO should be transferred from the S_1 level of TTA. The following question is whether the energy can transfer from the T_1 level of TAPO to that of TTA. Another TRES with the time range from 0.2 to 1.6 μs were measured (Fig. 7), which consist of two kinds of emission peaks. The emissions from 400 to 500 nm are recognized as $Ph_{TAPO\mathbf{1}}$, and the other emissions around 530 nm correspond to the phosphorescent emission of TTA ($Ph_{TTA\mathbf{1}}$). It is noticeable that from 0.2 to 1.6 μs the intensity of $Ph_{TAPO\mathbf{1}}$ gradually decreases. Simultaneously, $Ph_{TTA\mathbf{1}}$ becomes stronger and stronger. There is a corresponding relation between them that the decline of $Ph_{TAPO\mathbf{1}}$ is accompanied by the growth of $Ph_{TTA\mathbf{1}}$. Thus, although part of the energy transfers to the T_1 level of TTA through intersystem crossing (ISC) from the S_1 level of TTA, the Dexter-type energy transfer between the T_1 levels of TAPO and TTA should be another efficient channel.

The energy transfer between the S_1 level of TTA and the T_1 level of TAPO belongs to the singlet–triplet (S–T) energy transfer, which is overall a spin-forbidden process. Spin is flipped between the initial state $^1(^1D^{*1}A)$ and the final state $^3(^1D^3A^*)$. Herein, donor (D) is TTA and acceptor (A) is TAPO. However, in lanthanide complexes, S–T energy transfer is promoted via the spin-orbit coupling terms in the Hamiltonian. It is now well established that if the triplet energy level was involved in, the energy transfer depends on the degree of orbital overlap between donor and acceptor. Therefore, the S–T coupling can be given by the approximate expression referring to T–T coupling [23,25]:

$$V^{S-T} = \frac{2\beta_{ET}2\beta_{HT}}{{}^3A} - Z \qquad (2)$$

where β_{ET} is the electron transfer matrix element between donor and acceptor, β_{HT} is the corresponding hole transfer matrix element, ^3A is the energy gap between the singlet excited ($^1D^*$) configurations and triplet excited ($^3A^*$) configurations, and Z is the two-electron exchange integral. The ^3A between TTA and TAPO is appropriate as ~0.3 eV.

The Dexter exchange integral is [24,25]

$$Z = \sum_{i,j}\sum_{r,s} c_i c_j c_r c_s (ir|js) \qquad (3)$$

The energy transfer rate is exponentially attenuated with the overlap of electron clouds. Usually the distance-dependence of experimentally measured Dexter energy transfer rates is characterized following $k_D = A' \exp(-\beta R)$ [26]. R is the distance between donor and acceptor. According to the time-resolved experimental data, k_D of the energy transfer from the S_1 level of TTA to the T_1 level of TAPO is about 8.33×10^5.

For comparison, the intramolecular energy transfer processes of $Eu(TTA)_3(TPPO)_2$ and **1** are shown as followed:

$$\begin{tikzcd}
 & S_1^{TTA} \arrow[r] & T_1^{TTA} \arrow[dr] & \\
S_1^{TPPO} \arrow[ur] \arrow[dr] & & & {}^5D_0^{Eu^{3+}} \\
 & T_1^{TPPO} \arrow[uur] & &
\end{tikzcd}
\qquad
\begin{tikzcd}
 & S_1^{TTA} \arrow[r] \arrow[d] & T_1^{TTA} \arrow[dr] & \\
S_1^{TAPO} \arrow[ur] \arrow[dr] & T_1^{TAPO} \arrow[ur] & & {}^5D_0^{Eu^{3+}} \\
 & & &
\end{tikzcd}$$

For $Eu(TTA)_3(TPPO)_2$, firstly TPPO is excited to its S_1 level, then one part of the energy transfers to the S_1 level of TTA, and then transferred to the T_1 levels of TTA. The other part of the S_1 energy of TPPO transfers to the T_1 level of TPPO directly. Finally, the triplet energy converges to $^5D_0$ of Eu^{3+}. However, for **1**, after exciting TAPO to its S_1 level, the energy transfers to the S_1 level of TTA and the T_1 level of TAPO, respectively. Then the energy is further respectively transferred to the T_1 levels of TAPO and TTA from the S_1 level of TTA, as proved above. Subsequently, all the energy is converged to the T_1 level of TTA, and finally transferred to $^5D_0$ of Eu^{3+}. Notably, because TAPO possesses the intermediate T_1 level, the intramolecular energy transfer process is from the S_1 level of TAPO to $^5D_0$ of Eu^{3+} through the S_1 level of TTA and the T_1 levels of TAPO and TTA step by step. This kind of stepwise process makes intramolecular energy transfer more efficient, and is one of the most important factors resulting in the great improvement of the luminescent performance of **1**.

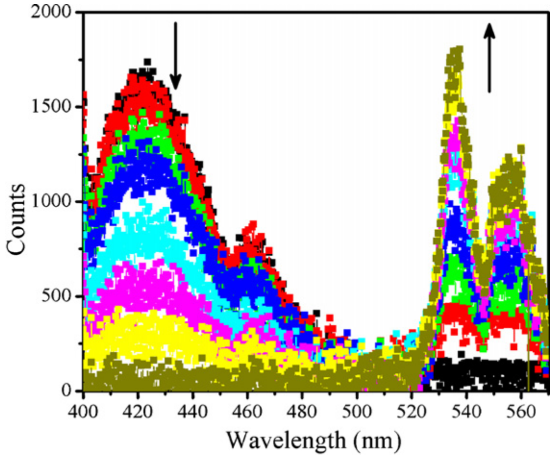


Fig. 7. Time-resolved emission spectra of **1** in CH_2Cl_2 between 0.2 and 1.6 μs with a time interval of 0.2 μs and the excitation wavelength of 380 nm at room temperature.

4. Conclusion

In this work the intramolecular energy transfer process in the ternary Eu^{3+} complex was studied in detail. Our investigation shows that when the neutral ligand like TAPO has an appropriate T_1 level between the S_1 and T_1 levels of the anion ligand TTA, the Dexter-type energy transfer can occur from the S_1 level of TTA to the T_1 level of TAPO. Therefore, the intramolecular energy transfer process in **1** is from the S_1 level of TAPO to $^5D_0$ of Eu^{3+} step by step: $S_1^{TAPO} \to S_1^{TTA} \to T_1^{TAPO} \to T_1^{TTA} \to {}^5D_0^{Eu^{3+}}$. This kind of stepwise process makes intramolecular energy transfer more efficient, which is one of the most important factors resulting in the great improvement of PL performance of **1**. It is shown that in the ternary systems the efficient energy transfer between the neutral and anion ligands is crucial to the luminescent performance of the complex. Moreover, the ladder-like distribution of the excited energy levels is more advantageous. Thus, through designing neutral ligands with the appropriate S_1 and T_1 levels, the efficiency of intramolecular energy transfer can be improved greatly. It is referrible in designing high-performance light-emitting lanthanide complexes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.10.011.

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